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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Radiation-Curable Oligomers and Liquid,
Radiation-Curable Coating Composition for Coating Glass
Surfaces

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Notice: This application is as filed and may therefore contain an
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FILE, PIN IN THIS AMENDED
TEXT TRANSLATION

1460Z

5 BASF Lacke + Farben Aktiengesellschaft

Radiation-curable oligomers and liquid, radiation-
curable coating composition for coating glass surfaces

10 The present invention relates to radiation-
curable oligomers having two or more ethylenically
unsaturated end groups and two or more urea and
possibly urethane groups per molecule, which oligomers
can be prepared from

15

- a) at least one hydroxy- and/or amino-functional com-
pound with a functionality of between 3 and 4,
- b) at least one compound with 2 hydroxyl and/or amino
groups per molecule,
- 20 c) at least one monoethylenically unsaturated com-
pound with a group having one active hydrogen atom
per molecule and with a number-average molecular
weight of between 116 and 1000, and
- d) at least one aliphatic and/or cycloaliphatic
25 diisocyanate,

components a to d being employed in amounts such that

- 1.) the molar ratio of component a to component b is
30 between 0.1:1 and 1.1:1,

- 2.) the molar ratio of component c to component a is between 2:1 and 10:1, and
- 3.) the ratio of equivalents of the isocyanate groups of component d to the amino and possibly hydroxyl groups in the sum of components a to c is between 0.9 and 1.0.

The present invention also relates to radiation-curable coating compositions containing these radiation-curable oligomers and to processes for coating glass surfaces, especially optical glass fibers, in which these coating compositions are employed.

Optical glass fibers have gained continually increasing importance in the communications sector as optical waveguide fibers. For this application it is absolutely necessary to protect the glass surface from moisture and wear phenomena. Consequently the glass fibers are provided directly after their production with at least one protective coating.

Thus it is known from EP-B-114 982, for example, to provide glass fibers initially with a buffer coat (primer) which is elastic but not very hard and not very tough, based on linear urethane acrylates, and subsequently to apply a radiation-curable topcoat which is likewise based on linear urethane acrylates and which is of high hardness and toughness. The two-coat structure is intended to provide protection to the glass fibers under mechanical loading, even at low

temperatures. However, coatings based on linear urethane acrylates have the disadvantage that the mechanical properties of the coatings, especially their elasticity, are still in need of improvement.

5 Furthermore, EP-A-223 086 also discloses radiation-curable coating compositions for coating optical glass fibers. These coating compositions contain as binder radiation-curable oligomers which can be prepared from polyethertriols or -triamines having an
10 average molecular weight of from 300 to 4000, polyetherdiols or -diamines having an average molecular weight of from 200 to 4000, OH-functional acrylate monomers and diisocyanates, where the oligomers are prepared employing a molar ratio of triol or triamine
15 to diol or diamine of between 2.5:1 and 20:1. These radiation-curable coating compositions described in EP-A-223 086 are employed either as a topcoat or as a one-coat finish. As a primer, however, they are unsuitable because the fully cured coatings have an
20 excessive modulus of elasticity.

 EP-A-209 641 also describes radiation-curable coating compositions for coating optical glass fibers. These coating compositions contain as binder a polyurethane oligomer with acrylate end groups which is
25 based on a polyfunctional core. These coating compositions can be used both as primer and as topcoat. One-coat processing is also possible.

 The international patent application with the
Publication Number WO 92/04391 discloses

radiationcurable coating compositions for coating optical glass fibers, which contain as binder radiation-curable oligomers in accordance with the precharacterizing clause of the main claim. Because of their low modulus of elasticity, these coating compositions are employed in particular as primers for glass fibers. However, the manufacturers of optical glass fibers require a further improvement in the mechanical properties of the coatings. In particular, the buffer action of the coatings should be optimized further, and the buffer properties should remain as constant as possible over a broad temperature range. At the same time, the reactivity of the coating compositions should not be impaired and the ease of assembly of the coated glass fibers should be ensured.

The object on which the present invention is based is to provide radiation-curable coating compositions for coating glass surfaces, especially optical glass fibers, which lead to coatings having properties which are improved in comparison with the known coating compositions. In particular, the fully cured coatings should exhibit an improved buffer action through lower moduli of elasticity at higher elongations at break, and the buffer properties should remain approximately the same over as great a temperature range as possible. This means that any impairment of the mechanical properties of the coating as the temperature falls should be minimized. In particular, there should only be a minimal increase in the modulus of elasticity as

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the temperature falls. At the same time the coating compositions should cure fully as quickly as possible. Moreover, the coating compositions should enable improved assembly of the coated glass fibers. It is
5 therefore necessary, especially at the junctions between different glass fibers, that the coatings have a reduced adhesion to the glass fiber so that they can be removed easily in the junction area. On the other hand, however, the adhesion of the coating to the glass
10 fiber should not deteriorate excessively on exposure to moisture, in order to ensure that no delamination occurs by exposure to moisture as the optical fibers age.

The object is surprisingly achieved by radiation-curable oligomers with two or more ethylenically
15 unsaturated end groups and two or more urea and possibly urethane groups per molecule, which can be prepared from

- 20 a) at least one hydroxy- and/or amino-functional compound with a functionality of between 3 and 4,
- b) at least one compound with 2 hydroxyl and/or amino groups per molecule,
- c) at least one monoethylenically unsaturated compound with a group having one active hydrogen atom
25 per molecule and with a number-average molecular weight of between 116 and 1000, and
- d) at least one aliphatic and/or cycloaliphatic diisocyanate,

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components a to d being employed in amounts such that

1. the molar ratio of component a to component b is
between 0.1:1 and 1.1:1, preferably between 0.1
5 and 0.8,
2. the molar ratio of component c to component a is
between 2.0:1 and 10:1, preferably between 2.5 and
10, and
3. the ratio of equivalents of the isocyanate groups
10 of component d to the amino and possibly hydroxyl
groups in the sum of components a to c is between
0.9 and 1.0.

The radiation-curable oligomers are characterized in
15 that

- 1.) as component a at least one amino group-containing
compound a_1 having a number-average molecular
weight of more than 4000 to 10,000 and/or at least
20 one amino and/or hydroxyl group-containing com-
pound a_2 having a number-average molecular weight
of from 400 to 4000 has been employed,
- 2.) as component b at least one amino group-containing
compound b_1 having a number-average molecular
25 weight of more than 4000 to 10,000 and/or at least
one amino and/or hydroxyl group-containing com-
pound b_2 having a number-average molecular weight
of from 200 to 4000 has been employed,

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3.) the oligomers have double bond contents of from
0.25 to 0.44 mol/kg, and

4.) in the preparation of the oligomers at least one
amino group-containing compound a_1 and/or b_1 has
5 been employed.

The present invention also relates to
radiation-curable coating compositions containing these
radiation-curable oligomers, and to processes for
10 coating glass surfaces, especially optical glass
fibers, in which these coating compositions are
employed.

It is surprising and was not foreseeable that
radiation-curable coating compositions based on the
15 oligomers according to the invention lead to coatings
having a buffer action which is improved in relation to
conventional coatings, i.e. having lower moduli of
elasticity coupled with greater elongations at break. A
further advantage is a good buffer action of the
20 coatings even at low temperatures, since this solves
the problem of so-called microflexions. The coatings
according to the invention are further distinguished by
good mechanical properties, such as, for example, elon-
gation and tensile strength adapted to the application,
25 and by reduced adhesion of the coatings to the glass
fiber, enabling improved assembly of the coated glass
fibers. At the same time the adhesion of the coating
does not deteriorate excessively after exposure to
moisture, so that it is ensured that no delamination

exposure to moisture as the optical fibers age. Finally, the coating compositions according to the invention are quick to cure fully.

There now follows a closer description,
5 initially, of the radiation-curable oligomers according to the invention:

It is essential to the invention that the oligomers are prepared employing amino group-containing compounds a_1 having a functionality of from 3 to 4 and
10 having a number-average molecular weight of more than 4000 to 10,000, preferably of more than 4000 to 6000, and/or difunctional, amino group-containing compounds b_1 having a number-average molecular weight of more than 4000 to 10,000, preferably of more than 4000 to
15 6000. The compounds preferably employed as component a_1 and/or component b_1 are those having secondary amino groups, in particular polyethers having terminal, secondary amino groups. Particular preference is given to the employment, as component a_1 , of polyalkoxylated
20 triols having terminal, secondary amino groups. Examples of compounds which are suitable as component a_1 and have primary amino groups are the amino-functional compounds derived from polyalkoxylated triols, for example the products which are commercially
25 available from Texaco under the name JEFFAMIN®, e.g. JEFFAMIN® T 5000.

The secondary amines employed as component a_1 can be prepared, for example, by reacting the corresponding polyethers, containing primary amino groups, with

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aliphatic ketones such as, in particular, methyl isobutyl ketone and subsequently hydrogenating the resulting ketimine. Examples of polyethers which contain primary amino groups and are suitable for this
5 reaction are the products available from Texaco under the name JEFFAMIN®, such as JEFFAMIN® T 5000.

Also suitable as component a₁ are the products commercially available from CONDEA Chemie GmbH under the name NOVAMIN®, e.g. NOVAMIN® N 60.

10 Examples of compounds employed as component b₁ are the amino-functional compounds available from Texaco under the name JEFFAMIN® and derived from polyalkoxylated diols, such as, for example, JEFFAMIN® D 4000. The secondary amines employed as component b₁
15 can be prepared analogously to the compounds a₁ by reacting the corresponding polyethers which contain primary amino groups with aliphatic ketones such as, in particular, methyl isobutyl ketone and subsequently hydrogenating the resulting ketimine. Examples of
20 polyethers which contain primary amino groups and are suitable for this reaction are the JEFFAMIN® grades listed under b₁.

Also suitable as component b₁ are the products commercially available from CONDEA Chemie GmbH under
25 the name NOVAMIN®, e.g. NOVAMIN® N 50.

It is particularly preferred to employ as component b₁ polyalkoxylated diols having terminal, secondary amino groups.

It is also possible if desired, for the preparation of the oligomers according to the invention, to employ further amino and/or hydroxyl group-containing compounds a_2 having a functionality of from 3 to 4, preferably 3, and having a number-average molecular weight of from 400 to 4000, preferably from 750 to 2000.

Examples of suitable amino and/or hydroxyl group-containing compounds a_2 are polyoxyalkylated triols, for example ethoxylated and propoxylated triols, preferably ethoxylated triols particularly preferably having a number-average molecular weight of greater than or equal to 1000. Examples of triols which are employed are glycerol or trimethylolpropane.

Also suitable as component a_2 are the corresponding amino-functional compounds, for example the amino-functional compounds derived from polyalkoxylated triols. Examples are the products available from Texaco under the name JEFFAMIN®, for example JEFFAMIN®, T 403 and T 3000 and the products available from CONDEA Chemie GmbH under the name NOVAMIN®, e.g. NOVAMIN® N 30.

In this context the amino-functional compounds a_2 may contain both primary and secondary amino groups. Suitable compounds in addition to these are also those containing both amino and hydroxyl groups.

It is also possible if desired, for the preparation of the oligomers according to the invention, to employ further amino and/or hydroxyl

group-containing compounds b₂ containing two hydroxyl and/or amino groups per molecule.

These compounds b₂ have number-average molecular weights of from 200 to 4000, preferably from 600 to
5 2000.

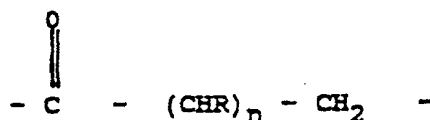
Examples of suitable amino and/or hydroxyl group-containing compounds b₂ are polyoxyalkylene glycols and polyoxyalkylenediamines, in which alkylene groups containing from 1 to 6 C atoms are preferred.
10 Suitable examples are thus polyoxyethylene glycols having a number-average molecular weight of 1000, 1500, 2000 or 2500 and polyoxypropylene glycols having the corresponding molecular weights, and polytetramethylene glycols. Polyethoxylated and polypropoxylated diols can
15 also be employed, for example the ethoxylated or propoxylated derivatives of butanediol, hexanediol etc. It is also possible to employ polyesterdiols which can be prepared by, for example, reacting the glycols already mentioned with dicarboxylic acids, preferably
20 aliphatic and/or cycloaliphatic dicarboxylic acids, for example hexahydrophthalic acid, adipic acid, azelaic, sebacic and glutaric acid and/or their alkyl-substituted derivatives. Instead of these acids it is also possible to use their anhydrides where these exist.

25 Polycaprolactonediolis can also be employed. These products are contained [sic] by, for example, reacting an ϵ -caprolactone with a diol. Products of this kind are described in US-A 3 169 945.

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The polylactonedioles obtained by this reaction are distinguished by the presence of a terminal hydroxyl group and by recurring polyester units derived from the lactone. These recurring molecular units may
5 conform to the formula

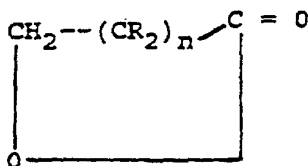


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in which n is preferably from 4 to 6 and the substituent is hydrogen, an alkyl radical, a cycloalkyl radical or an alkoxy radical, no substituent containing
15 more than 12 carbon atoms and the total number of carbon atoms of the substituents in the lactone ring not exceeding 12.

The lactone used as starting material may be any desired lactone or any desired combination of
20 lactones, and said lactone should contain at least 6 carbon atoms in the ring, for example from 6 to 8 carbon atoms, and there should be at least 2 hydrogen substituents on the carbon atom. The lactone used as starting material may be represented by the following
25 general formula:

5



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in which n and R have the meaning already indicated. The lactones which are preferred in the invention, for the preparation of the polyesterdiols, are the caprolactones in which n has the value 4. The most preferred

15 lactone is the substituted ϵ -caprolactone in which n has the value 4 and all the substituents R are hydrogen. This lactone is particularly preferred because it is available in large quantities and gives coatings having excellent properties. It is also

20 possible to make use of various other lactones, individually or in combination. Examples of aliphatic diols which are suitable for the reaction with the lactone are the diols already listed above for the reaction with the carboxylic acids.

25

It is of course also possible to employ as component b₂ the corresponding diamines and compounds having an OH and an amino group. Examples of suitable compounds are the products available from Texaco under the name JEFFAMIN D 230, D 400, D 2000, ED 600,

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ED 900, ED 2001, ED 4000, BUD 2000 and C 346 and the products available from CONDEA Chemie GmbH under the name NOVAMIN®, e.g. NOVAMIN® N 10, N 20 and N 40.

It is preferred to employ as component b₂ a
5 mixture of

b₂₁) from 0 to 90 mol% of at least one polyetherdiol
and

b₂₂) from 10 to 100 mol% of at least one modified
10 polyetherdiol composed of

- α) at least one polyetherdiol
- β) at least one aliphatic and/or cycloaliphatic dicarboxylic acid and
- 15 γ) at least one aliphatic, saturated compound having one epoxide group and having from 8 to 21 C atoms per molecule,

the sum of the proportions of components b₂₁ and b₂₂
20 and the sum of the proportions of components α to γ being in each case 100 mol%.

To prepare the modified polyetherdiols by conventional methods components α to γ are employed in amounts such that the ratio of equivalents of the OH
25 groups of component α to the carboxyl groups of component β is between 0.45 and 0.55, preferably 0.5, and the ratio of equivalents of the epoxide groups of component γ to the carboxyl groups of component β is between 0.45 and 0.55, preferably 0.5.

Examples of suitable polyetherdiols b_{21} and α are the polyoxyalkylene glycols already listed, in which the alkylene groups have from 1 to 6 C atoms. In this context it is preferred to employ as component b_{21} polyoxypropylene glycols having a number-average molecular weight of between 600 and 2000. As component α it is preferred to employ polyoxybutylene glycols (poly-TEF) having a number-average molecular weight > 1000.

10 The aliphatic and cycloaliphatic dicarboxylic acids which it is preferred to employ as component β are those having from 8 to 36 C atoms per molecule, for example hexahydrophthalic acid. Suitable examples for component γ are epoxidized, monoolefinically
15 unsaturated fatty acids and/or polybutadienes.

It is preferred to employ as component γ glycidyl esters of branched monocarboxylic acids, for example the glycidyl ester of versatic acid.

The compounds a_1 , a_2 , b_1 and b_2 are preferably
20 employed in amounts such that the molar ratio of the hydroxyl and/or amino groups of components a_2 and b_2 to the amino groups of components a_1 and b_1 is between 0 and 10, preferably between 0.1 and 3.

The compounds employed to introduce the
25 ethylenically unsaturated groups into the polyurethane oligomer are monoethylenically unsaturated compounds having one group containing an active hydrogen atom, which have a number-average molecular weight of from 116 to 1000, preferably from 116 to 400. Examples of

suitable components c which may be mentioned are, for example, hydroxyalkyl esters of ethylenically unsaturated carboxylic acids, for example hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyamyl acrylate, hydroxyhexyl acrylate and hydroxyoctyl acrylate, and the corresponding hydroxyalkyl esters of methacrylic, fumaric, maleic, itaconic crotonic and isocrotonic acid, but with the hydroxyalkyl esters of acrylic acid being preferred.

Also suitable as component c are adducts of caprolactone and one of the abovementioned hydroxyalkyl esters of ethylenically unsaturated carboxylic acids. It is preferred to employ adducts of hydroxyalkyl esters of acrylic acid having a number-average molecular weight of from 300 to 1000.

Suitable as component d for the preparation of the oligomers according to the invention are aliphatic and/or cycloaliphatic diisocyanates, for example 1,3-cyclopentane, 1,4-cyclohexane and 1,2-cyclohexane diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate) and isophorone diisocyanate, trimethylene, tetramethylene, pentamethylene, hexamethylene and trimethylhexamethylene 1,6-diisocyanate and the diisocyanates described in EP-A-204 161, column 4, lines 42 to 49 and are derived from dimeric fatty acids.

Isophorone diisocyanate and trimethylhexamethylene 1,6-diisocyanate are preferably employed.

Components a to d are employed for the preparation of the oligomers in amounts such that

1. the molar ratio of component a to component b is between 0.1:1 and 1.1:1, preferably between 0.1 and 0.8,
2. the molar ratio of component c to component a is
5 between 2.0:1 and 10:1, preferably between 2.5 and 10, and
3. the ratio of equivalents of the isocyanate groups of component d to the active hydrogen atoms of components a plus b plus c is between 0.9 and 1.0.

10

The oligomers according to the invention can be prepared in various ways. For instance, it is possible for example first to react the diisocyanate d with the chain-lengthening agents a and b and subsequently to
15 react the remaining free isocyanate groups with the ethylenically unsaturated compound c.

It is also possible to prepare the oligomers by first reacting some of the isocyanate groups of component d with the ethylenically unsaturated compound
20 c and by subsequently reacting the remaining free isocyanate groups with the chain-lengthening agents a and b.

It is also possible to prepare the polyurethane oligomers by the processes described on page 5 of
25 EP-A-223 086.

The polyurethane oligomers are preferably prepared by means of a two-stage process in which first of all the stoichiometric polyaddition of components a to d is carried out until more than 85% of the NCO groups

of component d have reacted. In this first process step, components a to d are employed in amounts such that the ratio of equivalents of the NCO groups of component d to the active hydrogen atoms of components a to c is 1:1.

In a second process step, the remainder of the other components (corresponding to the desired NCO:OH ratio) is then added and the reaction is continued up to a conversion of the NCO groups of > 99%. In this second process step it is preferred to add further component c and to adjust the desired NCO:OH ratio of equivalents by adding this component c. In this preferred two-stage process, it is preferred to employ as component c an adduct of hydroxyethyl acrylate and caprolactone having a number-average molecular weight of ≥ 300 .

It is essential to the invention that the urethane oligomers have double bond contents of from 0.25 to 0.44 mol/kg, preferably from 0.3 to 0.44 mol/kg. Furthermore, the urethane oligomers according to the invention generally have number-average molecular weights of from 2000 to 20,000, preferably from 3500 to 16,000 (measured by GPC against polystyrene standard), weight-average molecular weights of from 8000 to 100,000, preferably from 10,000 to 40,000 (measured by GPC against polystyrene standard) and a functionality of from 2 to 4, preferably from 2.5 to 3.0, in each case p r statistical average polymer molecule.

The oligomers according to the invention are employed as film-forming component A in radiation-curable coating compositions. The coating compositions conventionally contain from 10 to 78% by weight, preferably at least 15% by weight and particularly preferably from 63 to 73% by weight, based in each case on the total weight of the coating composition, of these oligomers according to the invention.

As a further component, the coating compositions may contain from 0 to 60% by weight, preferably from 0 to 50% by weight, based in each case on the total weight of the coating composition, of at least one further ethylenically unsaturated oligomer B. In addition to unsaturated polyesters, polyester acrylates and acrylate copolymers it is above all urethane acrylate oligomers which are employed, with the exception of the urethane acrylate oligomers employed as component A. The properties of the fully cured coating can be controlled specifically by the nature and amount of this component B. The higher the proportion of this component B, the higher in general the modulus of elasticity of the fully cured coating. Component B is consequently added to the coating compositions in particular when the coating compositions are employed as topcoat. The effect of this component B on the properties of the resulting coating is, however, known to those skilled in the art. The most favorable amount to be used in each case can therefore be readily determined on the basis of a few routine experiments. These

ethylenically unsaturated polyurethanes which are employed as component B are known. They can be obtained by reacting a di- or polyisocyanate with a chain-lengthening agent from the group comprising
5 diols/polyols and/or diamines/polyamines and subsequently reacting the remaining free isocyanate groups with at least one hydroxyalkyl acrylate or hydroxyalkyl ester of other ethylenically unsaturated carboxylic acids.

10 In this context, the amounts of chain-lengthening agent, di- or polyisocyanate and hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid are chosen such that

- 15 1. the ratio of equivalents of the NCO groups to the reactive groups of the chain-lengthening agent (hydroxyl, amino and/or mercaptyl [sic] groups) is between 3:1 and 1:2, preferably 2:1, and
2. the OH groups of the hydroxyalkyl esters of the
20 ethylenically unsaturated carboxylic acids are present in a stoichiometric quantity in relation to the remaining free isocyanate groups of the prepolymer composed of isocyanate and chain-lengthening agent.

25

It is furthermore possible to prepare the polyurethanes B by first reacting some of the isocyanate groups of a di- or polyisocyanate with at least one hydroxyalkyl [sic] ester of an ethylenically

unsaturated carboxylic acid and then by reacting the remaining isocyanate groups with a chain-lengthening agent. In this case, too, the amounts of chain-lengthening agent, isocyanate and hydroxyalkyl ester of unsaturated carboxylic acids are chosen such that the ratio of equivalents of the NCO groups to the reactive group of the chain-lengthening agent is between 3:1 and 1:2, preferably 2:1, and the ratio of equivalents of the remaining NCO groups to the OH groups of the hydroxylalkyl ester is 1:1.

Additional possibilities are of course all intermediate forms of these two processes. For example, some of the isocyanate groups of a diisocyanate can first be reacted with a diol, subsequently some more of the isocyanate groups can be reacted with the hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid, and following this the remaining isocyanate groups can be reacted with a diamine.

These various preparation processes of the polyurethanes are known (cf. for example EP-A-294 161) and consequently require no more detailed description.

Compounds which are suitable for the preparation of these urethane acrylate oligomers B are the compounds already employed in the preparation of component A, and also the compounds mentioned in DE-A 38 40 644.

Especially when using the coating compositions according to the invention as a topcoat, it is preferred to employ aromatic structural components for the

preparation of the urethane acrylate oligomers. Particularly preferred in this case are 2,4- and 2,6-toluylene diisocyanate as isocyanate component and aromatic polyesterpolyols based on phthalic acid and isophthalic acid and/or polypropylene glycol, ethylene [sic] glycol and diethylene glycol as chain-lengthening agents.

As a further component, the radiation-curable coating compositions also contain at least one ethylenically unsaturated monomeric and/or oligomeric compound C, generally in a quantity of from 20 to 50% by weight, preferably from 22 to 35% by weight, based in each case on the total weight of the coating composition.

By the addition of this ethylenically unsaturated compound C the viscosity and the curing rate of the coating compositions and the mechanical properties of the resulting coating are controlled, as is familiar to those skilled in the art and described in, for example, EP-A-223 086, to which reference is made in respect of further details.

Examples which may be mentioned of monomers which can be employed are ethoxyethoxyethyl acrylate, N-vinylcaprolactam, N-vinylpyrrolidone, phenoxyethyl acrylate, dimethylaminoethyl acrylate, hydroxyethyl acrylate, butoxyethyl acrylate, isobornyl acrylate, dimethylacrylamide and dicyclopentyl acrylate. Also suitable are di- and polyacrylates, for example butanediol diacrylate, hexanediol diacrylate, trimethylol-

propane di- and triacrylate, pentaerythritol tri- and tetraacrylate, the analogous acrylates of alkoxyated, in particular ethoxylated and propoxylated, polyols, for example glycerol, trimethylolpropane and penta-
5 erythritol, having a number-average molecular weight of from 266 to 1014, and the long-chain linear diacrylates described in EP-A-250 631 and having a molecular weight of from 400 to 4000, preferably from 600 to 2500. The two acrylate groups may, for example, be separated by a
10 polyoxybutylene structure. It is also possible to employ 1, 12-dodecyl diacrylate and the reaction product of 2 moles of acrylic acid with one mole of a dimeric fatty alcohol which in general has 36 C atoms.

Also suitable are mixtures of the monomers just
15 described. It is preferred to employ phenoxyethyl acrylate, hexanediol diacrylate, N-vinylcaprolactam and tripropylene glycol diacrylate.

The photoinitiator, conventionally employed in the coating compositions according to the invention in
20 an amount of from 2 to 8% by weight, preferably from 3 to 5% by weight, based on the total weight of the coating composition, varies with the radiation which is employed to cure the coating compositions (UV radiation, electron beam, visible light). The coating compositions according to the invention are preferably cured
25 using UV radiation. In this case, it is usual to employ photoinitiators based on ketones, for example acetophenone, benzophenone, α,α -dimethyl- α -hydroxyacetophenone, diethoxyacetophenone, 2-hydroxy-2-methyl-

1-phenylpropan-1-one, hydroxypropyl phenyl ketone, m-chloroacetophenone, propiophenone, benzoin, benzil, benzil dimethyl ketal, anthraquinone, thioxanthone and thioxanthone derivatives and triphenylphosphine and the
5 like, and also mixtures of different photoinitiators.

In addition, coating compositions may if desired also contain conventional auxiliaries and additives. These are employed conventionally in an amount of from 0 to 4% by weight, preferably from 0.5 to 2.0%
10 by weight, based in each case on the total weight of the coating composition. Examples of such substances are leveling agents and plasticizers.

The coating compositions can be applied to the substrate using known application methods, for example
15 spraying, rolling, flow coating, immersion, knife coating or brushing.

The coating films are cured using radiation, preferably using UV radiation. The apparatus and conditions for these curing methods are known from the
20 literature (cf. e.g. R. Holmes, U.V. and E.B. Curing Formulations for Printing Inks, Coatings and Paints, SITA Technology, Academic Press, London, United Kindom [sic] 1984) and require no further description.

The coating compositions are suitable for
25 coating a variety of substrates, for example glass, wood, metal and plastic surfaces. However, they are employed in particular for coating glass surfaces, especially preferably optical glass fibers.

The present invention therefore also relates to a process for coating a glass surface, in which a radiation-curable coating composition is applied and is cured by means of UV radiation or electron beams, which is characterized in that the coating compositions according to the invention are employed as radiation-curable coating composition.

The process according to the invention is particularly well suited to the coating of optical glass fibers. In this context the coating compositions according to the invention may be applied to the glass fibers, in particular, as primer, but if desired also as the topcoat of a two-coat finish. When using the coating compositions as primer, the fully cured coatings usually have a modulus of elasticity (at 2.5% elongation and room temperature) of less than 10 MPa.

When using the coating compositions as topcoat, the fully cured coatings usually have a modulus of elasticity (at 2.5% elongation and room temperature) of from 500 to 1000 MPa.

The invention is illustrated in more detail in the following examples. All data on parts and percentages are data by weight, unless expressly stated otherwise.

Preparation of a modified polyetherdiol

In a vessel fitted with stirrer, inert gas inlet and thermal sensor, 51.1 parts of polytetrahydrofuran having a number-average molecular weight of

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1000 and an OH number of 118 mg of KOH/g and 19.1 parts of hexahydrophthalic anhydride are heated to 120°C and maintained at this temperature until an acid number of 102 mg of KOH/g is reached. Then 0.02% of chromium
5 octoate [sic], based on the weight of the mixture of poly-THF, hexahydrophthalic acid and glycidyl ester of versatic acid and 29.7 parts of the glycidyl ester of versatic acid having an epoxide equivalent weight of 266 are added. The mixture is heated at 120°C until the
10 reaction product has an epoxide equivalent weight > 20,000, an acid number of 4 mg of KOH/g and an OH number of 60 mg of KOH/g.

The modified polyetherdiol has an average molecular weight $M_n = 1860$ (calculated from the OH
15 number), an M_n determined by GPC of ≈ 1500 and an $M_w/M_n = 1.67$. The viscosity of an 80% strength solution in butyl acetate is 3.8 dPas (measured at 23°C with a plate/cone viscometer).

20 Comparative Example 1

As described in Example 1 of International Patent Application WO 92/04391, 0.35 mol of a commercially available ethoxylated trimethylolpropane having a number-average molecular weight of 1014, 0.65 mol of
25 commercially available polyoxypropylene glycol having a number-average molecular weight of 600, 0.65 mol of the above-described modified polyetherdiol, 1.75 mol of hydroxyethyl acrylate, 0.05% of dibutyltin dilaurate (based on the total weight of the sum of components a,

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b, c and d), 0.1% of 2,6-di-tert-butylcresol (based on the total weight of the sum of components a, b, c and d) and 30 ppm of phenothiazine (based on the total weight of the sum of components a, b, c and d) are charged to a vessel provided with stirrer, feed devices, thermal sensor and air inlet, and heated to 60°C. Subsequently 2.70 mol of isophorone diisocyanate are metered in over a period of 2.5 h at 50°C. The mixture is then diluted with phenoxyethyl acrylate to a theoretical solids [lacuna] of 90% (sum of components a to d) and the temperature is maintained at 60°C until an NCO value of 1% is reached. Then 0.05% of dibutyltin dilaurate and 0.51 mol of a commercially available hydroxyethyl acrylate/caprolactone oligomer having a number-average molecular weight of 344 (commercial product TONE M 100 from Union Carbide) are added at a temperature of 80°C and the temperature is maintained at 80°C until an NCO value of < 0.1% is reached. The resulting oligomer has a double bond content of 0.6 mol/kg and a functionality of 2.5.

A 40% strength solution (based on the theoretical solids content) of the resulting oligomer 1 in phenoxyethyl acrylate has a viscosity of 4.9 dPas (measured at 23°C with a plate/cone viscometer).

A radiation-curable coating composition 1 is prepared by mixing 66.8 parts of the above-described urethane oligomer 1, 29.3 parts of phenoxyethyl acrylate and 3.9 parts of α,α -dimethyl- α -hydroxyacetophenone. Well-cleaned (above all grease-

free) glass plates (width x length = 98 x 161 mm) are taped at the edge with Tesakrepp® adhesive tape No. 4432 (width 19 mm) and the coating composition 1 is applied by knife coating (dry film thickness 180 μm).

5 Full curing is carried out using a UV irradiation unit fitted with two Hg medium-pressure radiators each with a lamp output of 80 W/cm, at a belt speed of 14 m/minute, in 1 pass under full-load operation.

The irradiation dose in this case is 0.15 J/cm²
10 (measured with the UVICURE dosimeter, system EIT from Eltosch).

The results of the determination of modulus of elasticity at 0.5 and 2.5% elongation (in accordance with the standard DIN 53 455) and the results of the elongation at break test are shown in Table 3. Also
15 shown in Table 3 are the glass transition temperature (measured using DMTA = Dynamic Mechanical Thermal Analysis) and the results of the adhesion test before and after exposure to moisture. The adhesion test in
20 this case was carried out in accordance with DIN Standard 53289.

Example 1

In the vessel described in Comparative Example
25 1, 1.3 mol of the above-described modified polyetherdiol, 1.75 mol of hydroxyethyl acrylate and 0.51 mol of a commercially available hydroxyethyl acrylate/caprolactone oligomer having a number-average molecular weight of 344 (commercial product TONE M 100 from Union

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Carbide) together with 0.05% of dibutyltin dilaurate (based on the total weight of the sum of components a, b, c and d), 0.1% of 2,6-di-tert-butylcresol (based on the total weight of the sum of components a, b, c and d) and 50 ppm of phenothiazine (based on the total weight of the sum of components a, b, c, d) are charged and heated to 60°C under a protective gas atmosphere (nitrogen/air = 3:1). Subsequently 2.70 mol of isophorone diisocyanate are metered in over a period of 2.5 h and the temperature is maintained at 60°C until an NCO value of 1.5% is reached. The mixture is then heated to 80°C and the temperature is maintained at 80°C until an NCO value of 0.9% (theoretically 0.82%) is reached. A 40% strength solution (based on the theoretical solids content) of the resulting product in phenoxyethyl acrylate has a viscosity of 3.6 dPas (measured at 23°C with a plate/cone viscometer). Then, at a temperature of 60°C, 0.35 mol of a commercially available propoxylated glycerol having on average 3 secondary amino groups per molecule (number-average molecular weight 5250, amino equivalent weight 2220 g, content of primary amino groups < 0.02 mmol/g, commercial product NOVAMIN® N60 from Condea Chemie GmbH) are metered in at a rate such that the temperature does not exceed 65°C. The temperature is maintained at 60°C until the NCO content is < 0.1% (adjust if necessary with < 10% of the starting quantity of polyethertriamine to an NCO content of < 0.1%). The resulting oligomer has a double bond content of

0.42 mol of double bonds/kg of oligomer and a functionality of 2.5 (average number $C = C/\text{molecule}$). A 40% strength solution (based on the theoretical solids content) of the resulting oligomer in phenoxyethyl acrylate has a viscosity of 4.1 dPas (measured at 23°C with a plate/cone viscometer).

In analogy to Comparative Example 1, a radiation-curable coating composition 2 is prepared by mixing 66.8 parts of the above-described urethane acrylate oligomer 2, 29.3 parts of phenoxyethyl acrylate and 3.9 parts of α, α -dimethyl- α -hydroxyacetophenone.

The application and curing of the coating composition 2 is carried out in analogy to Comparative Example 1. The test results of the resulting coating are shown in Table 3.

Example 2

In analogy to Example 1, a radiation-curable oligomer 3 was prepared with the only difference being that, instead of 0.35 mol of NOVAMIN® N 60, in this case 0.35 mol of a commercially available propoxylated glycerol having on average 3 primary amino groups per molecule were employed ($M_n = 5000$, amine equivalent weight 1890 g, commercial product JEFFAMIN® T 5000 from Texaco). After the addition of the isophorone diisocyanate, in this case the temperature was maintained at 60°C until an NCO value of 1.8% was reached. Subsequently the mixture was likewise heated to 80°C and the temperature was maintained at 80°C until an NCO

value of 0.9% was reached. A 40% strength solution of the resulting intermediate product has a viscosity of 2.9 dPas, measured at 23°C with a plate/cone viscometer using phenoxyethyl acrylate as solvent. The reaction
5 with the amine is carried out in analogy to Example 1. A 40% strength solution (based on the theoretical solids content) of the resulting oligomer 3 in phenoxyethyl acrylate has a viscosity of 5.1 dPas (23°C, plate/cone viscometer). The preparation,
10 application and curing of the coating composition 3 is carried out in analogy to Example 1. The test results of the resulting coating are shown in Table 3.

Comparative Example 2

15 In analogy to Example 1, a radiation-curable oligomer 4 was prepared with the difference being that, instead of 0.35 mol of the polyethertriamine having secondary amino groups (NOVAMIN® N 60), in Comparative
Example 2 0.35 mol of a commercially available
20 propoxylated glycerol having on average 3 primary amino groups per molecule and having a number-average molecular weight of 3000 was employed (amine equivalent weight 1060 g, commercial product JEFFAMIN® T 3000 from
Texaco). After the addition of the isophorone diiso-
25 cyanate, in this case the temperature was maintained at 60°C until an NCO value of 2.2% was reached. The mixture was then likewise heated to 80°C and the temperature was maintained at 80°C until an NCO value of 0.9% was reached. A 40% strength solution of the

resulting intermediate product of Comparative Example 2 has a viscosity of 2.7 dPas, measured at 23°C with a plate/cone viscometer using phenoxyethyl acrylate as solvent. The reaction with the amine is carried out in analogy to Example 1.

A 40% strength solution (based on the theoretical solids content) of the resulting oligomer in phenoxyethyl acrylate has a viscosity of 4.6 dPas, measured at 23°C with a plate/cone viscometer. The preparation, application and curing of the radiation-curable coating composition 4 is carried out in analogy to Example 1. The test results of the resulting coatings are shown in Table 3.

15 Example 3

In the vessel described in Comparative Example 1, 0.65 mol of the above-described modified polyetherdiol, 0.35 mol of a commercially available, ethoxylated trimethylolpropane having a number-average molecular weight of 1000, 1.75 mol of hydroxyethyl acrylate and 0.51 mol of a commercially available hydroxyethyl acrylate/caprolactone oligomer having a number-average molecular weight of 344 (commercial product TONE M 100 from Union Carbide) together with 0.05% of dibutyltin dilaurate (based on the total weight of components a, b, c and d), 0.1% of 2,6-di-tert-butylcresol (based on the total weight of components a, b, c and d) and 50 ppm of phenothiazine (based on the total weight of components a, b, c and d) are charged and heated to

60°C under a protective gas atmosphere (nitrogen/air = 3:1). Subsequently 2.70 mol of isophorone diisocyanate are metered in over a period of 2.5 h and the temperature is maintained at 60°C until
5 an NCO value of 1.5% is reached. A 50% strength solution of the resulting intermediate product in phenoxyethyl acrylate has a viscosity of 6.7 dPas (measured at 23°C with a plate/cone viscometer). Then, at a temperature of 60°C, 0.65 mol of a commercially
10 available propoxylated glycerol having on average 2 secondary amino groups per molecule (number-average molecular weight 4150, amine equivalent weight 2350 g, content of primary amino groups < 0.02 mmol/g, commercial product NOVAMIN® N 50 from Condea Chemie
15 GmbH) are metered in at a rate such that the temperature does not exceed 65°C. The temperature is maintained at 60°C until the NCO content is < 0.1% (adjust if necessary with < 10% of the starting amount of polyetherdiamine to an NCO content of < 0.1%). The
20 resulting oligomer 5 has a double bond content of 0.414 mol/kg and a functionality of 2.5. A 40% strength solution (based on the theoretical solids content) of the resulting oligomer in phenoxyethyl acrylate has a viscosity of 3.7 dPas (measured at 23°C with a
25 plate/cone viscometer).

The preparation, application and curing of the radiation-curable coating composition 5 is carried out in analogy to Example 1. The test results of the resulting coating are shown in Table 3.

Comparative Example 3

In analogy to Example 3, a radiation-curable oligomer is prepared with the only difference being that, instead of 0.65 mol of the polyetherdiamine
5 having secondary amino groups and having a number-average molecular weight of 4150 (NOVAMIN® N 50), in this case 0.65 mol of a commercially available polyoxypropylenediamine having primary amino groups and having a number-average molecular weight of 4000 was
10 employed (amine equivalent weight 2220 g, commercial product JEFFAMIN® D 4000 from Texaco).

A 40% strength solution (based on the theoretical solids content) of the resulting oligomer 6 in phenoxyethyl acrylate has a viscosity of 6.6 dPas
15 (measured at 23°C with a plate/cone viscometer). The preparation, application and curing of the coating composition is carried out in analogy to Example 1. The test results of the resulting coating are shown in Table 3.

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Table 1: Composition of the oligomers in moles

Example	Mw	I1	C1	I2	C2	I3	C3
eth. TMP	1000		0.35				
PE-triamine 1°	3000				0.35	0.35	0.35
PE-triamine 1°	5000			0.35			
PE-triamine 2°	5250	0.35					
Polyoxypropylene	600		0.65				
mod. PE	1860	1.30	0.65	1.30	1.30	0.65	0.65
PE-diamine 1°	4000						
PE-diamine 2°	4150					0.65	0.65
HEA	116	1.75	1.75	1.75	1.75	1.75	1.75
TONE M 100	344	0.51	0.51	0.51	0.51	0.51	0.51
IPDI	222	2.70	2.70	2.70	2.70	2.70	2.70

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In Table 1 the following abbreviations were used:

	eth. TMP:	ethoxylated trimethylolpropane
	PE-triamine 1°:	propoxylated glycerol with
5		primary amino groups
	PE-triamine 2°:	propoxylated glycerol with
		secondary amino groups
	mod. PE:	modified polyetherdiol
	PE-diamine 1°:	polyoxypropylenediamine with
10		primary amino groups
	PE-diamine 2°:	polyoxypropylenediamine with
		secondary amino groups
	HEA:	2-hydroxyethyl acrylate
	TONE M 100:	hydroxyethyl
15		acrylate/caprolactone oligomer
	IPDI:	isophorone diisocyanate

Table 2: Characteristics of the oligomers

	I1	C1	I2	C2	I3	C3
Molar ratio a/b	0.27	0.27	0.27	0.27	0.27	0.27
Molar ratio c/a	6.46	6.46	6.46	6.46	6.46	6.46
Molar ratio OH/NH (from a, b)	2.48	-	2.48	2.48	1.81	1.81
Ratio of equivalents NCO/(OH+NH) 1)	0.91	0.91	0.91	0.91	0.91	0.91
DBC [mol of C = C/kg]	0.42	0.745	0.422	0.498	0.414	0.422
Funct. [av. C = C/molecule]	2.5	2.5	2.5	2.5	2.5	2.5
Viscosity (40% in POEA 23°C) [dPas]	4.10	4.90	5.10	4.60	3.70	6.60

1) Calculated with the assumption that $\text{NH}_2 = \text{NH}$.

Table 3: Test results of the coatings (coating composition in each case from 66.8 parts by weight of urethane acrylate oligomer, 29.3 parts of phenoxyethyl acrylate and 3.9 parts of α,α -dimethyl- α -hydroxyacetophenone)

	I1	C1	I2	C2	I3	C3
Modulus of elasticity (0.5% elongation) [MPa]	0.99	3.04	1.22	1.43	0.74	1.04
Modulus of elasticity (2.5% elongation) [MPa]	1.02	2.94	1.21	1.49	0.79	1.12
Elongation at break [%]	58	27	51	38	58	55
Glass transition temp. Tg [°C]	-41	-19	-38	-31	-57	-51
Adhesion 50% rel. humidity [N]	0.80	0.40	0.40	0.40	0.37	0.60
95% rel. humidity [N]	0.40	0.20	0.30	0.20	0.20	0.30

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Summary of test results

As is evident from comparing Examples 1 and 2 with Comparative Examples 1 and 2 and from comparing Example 3 with Comparative Example 3, the use of amino group-containing chain-lengthening agents having a number-average molecular weight M_n of more than 4000 results in a distinct improvement in the buffer action of the resulting coating. Thus the coatings according to the invention of Examples 1 and 2 in comparison with the coating of Comparative Example 2 which has an analogous structure but was prepared only using an amino group-containing chain-lengthening agent having a number-average molecular weight of only 3000, exhibit distinctly decreased moduli of elasticity coupled with increased elongation at break and distinctly reduced glass transition temperatures, with the use of chain-lengthening agents having secondary amino groups (Example 1) bringing a further improvement in the mechanical properties of the coatings in comparison to chain-lengthening agents having primary amino groups (Example 2).

The comparison of Example 3 with the analogous Comparative Example 3 in which, instead of the amine according to the invention having a number-average molecular weight of 4150, in the latter case a primary amine having a number-average molecular weight of 4000 was employed, also confirms the improved mechanical properties of the coatings according to the invention.

Patent claims:

1. Radiation-curable oligomers with two or more ethylenically unsaturated end groups and two or more urea and possibly urethane groups per molecule, which
5 have been prepared from
- a) at least one amino- and/or hydroxy-functional compound with a functionality of between 3 and 4,
 - b) at least one compound with two hydroxyl and/or
10 amino groups per molecule,
 - c) at least one monoethylenically unsaturated compound with a group having one active hydrogen atom per molecule and with a number-average molecular weight of between 116 and 1000, and
 - 15 d) at least one aliphatic and/or cycloaliphatic diisocyanate,
- components a to d having been employed in amounts such that
- 20
- 1.) the molar ratio of component a to component b is between 0.1:1 and 1.1:1,
 - 2.) the molar ratio of component c to component a is between 2:1 and 10:1, and
 - 25 3.) the ratio of equivalents of the isocyanate groups of component d to the amino and possibly hydroxyl groups in the sum of components a to c is between 0.9 and 1.0,

characterized in that

- 1.) as component a at least one amino group-containing compound a_1 having a number-average molecular weight of more than 4000 to 10,000 and/or at least one amino and/or hydroxyl group-containing compound a_2 having a number-average molecular weight of from 400 to 4000 has been employed,
 - 2.) as component b at least one amino group-containing compound b_1 having a number-average molecular weight of more than 4000 to 10,000 and/or at least one amino and/or hydroxyl group-containing compound b_2 having a number-average molecular weight of from 200 to 4000 has been employed,
 - 3.) the oligomers have double bond contents of from 0.25 to 0.44 mol/kg, and
 - 4.) in the preparation of the oligomers at least one amino group-containing compound a_1 and/or b_1 has been employed.
2. Radiation-curable oligomers according to claim 1, characterized in that the oligomers have double bond contents of from 0.3 to 0.44 mol/kg.
 3. Radiation-curable oligomers according to claim 1 or 2, characterized in that as component a_1 amino group-containing compounds having a number-average molecular weight of more than 4000 to 6000 and/or as component b_1 amino group-containing [lacuna] of more than 4000 to 6000 have been employed.

4. Radiation-curable oligomers according to one of claims 1 to 3, characterized in that as component a₂ amino and/or hydroxyl group-containing compounds having a number-average molecular weight of from 750 to 2000
5 and/or as component b₂ amino and/or hydroxyl group-containing compounds having a number-average molecular weight of from 600 to 2000 and/or as component c compounds having a number-average molecular weight of between 116 and 400 have been employed.
- 10 5. Radiation-curable oligomers according to one of claims 1 to 4, characterized in that as component a₁ and/or b₁ compounds having secondary amino groups, preferably as component a₁ polyalkoxylated triols having terminal, secondary amino groups and/or
15 preferably as component b₁ polyalkoxylated diols having terminal, secondary amino groups have been employed.
6. Radiation-curable oligomers according to one of claims 1 to 5, characterized in that as component a₂ and/or b₂ hydroxyl group-containing compounds have been
20 employed.
7. Radiation-curable oligomers according to one of claims 1 to 6, characterized in that the molar ratio of the hydroxyl and/or amino groups of components a₂ and b₂ to the amino groups of components a₁ and b₁ is
25 between 0 and 10, preferably between 0.1 and 3.
8. Radiation-curable oligomers according to one of claims 1 to 7, characterized in that as component a₁ and/or a₂ compounds having a functionality of 3 have been employed.

9. Radiation-curable oligomers according to one of claims 1 to 8, characterized in that components a to d have been employed in amounts such that

- 5 1.) the molar ratio of component a to component b is between 0.1 and 0.8, and/or
2.) the molar ratio of component c to component a is between 2.5 and 10.

10. Radiation-curable coating composition, characterized in that it contains at least one radiation-curable oligomer according to one of claims 1 to 9.

11. Radiation-curable coating composition according to claim 10, especially for the buffer coating of optical glass fibers, characterized in that it contains

15

- A) from 10 to 78% by weight of at least one radiation-curable oligomer according to one of claims 1 to 9,
B) from 0 to 60% by weight of at least one further
20 ethylenically unsaturated oligomer,
C) from 20 to 50% by weight of at least one ethylenically unsaturated monomeric and/or oligomeric compound,
D) from 2 to 8% by weight of at least one photo-
25 initiator, and
E) from 0 to 4% by weight of conventional auxiliaries and additives,

the percentages by weight in each case relating to the total weight of the coating composition.

12. Radiation-curable coating composition according to claim 10, characterized in that it contains

5

A) at least 15% by weight of at least one radiation-curable oligomer according to one of claims 1 to 9,

10 B) from 0 to 50% by weight of at least one further ethylenically unsaturated oligomer,

C) from 22 to 35% by weight of at least one ethylenically unsaturated monomeric and/or oligomeric compound,

15 D) from 3 to 5% by weight of at least one photoinitiator, and

E) from 0.5 to 2.0% by weight of conventional auxiliaries and additives,

20 the percentages by weight in each case relating to the total weight of the coating composition.

13. Process for coating a glass surface, especially a glass fiber, in which

25 1) a radiation-curable primer is applied and is cured by means of UV radiation or electron beams, and

2) a radiation-curable topcoat is applied and is cured by means of UV radiation or electron beams,

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characterized in that as primer and/or topcoat a radiation-curable coating composition according to one of claims 10 to 12 is employed.

14. Optical glass fiber, characterized in that it
5 is coated with a radiation-curable coating composition according to one of claims 10 to 12.

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Liquid radiation-curable coating composition for
coating glass surfaces

Abstract

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The present invention relates to radiation-curable oligomers which can be prepared from polyether-triols or -triamines a, polyetherdiols or -diamines b, OH-functional acrylate monomers c and diisocyanates d, the molar ratio of a to b being between 0.1 to [sic] 1.1, the molar ratio of c to a being between 2.0 and 10 and the ratio of equivalents of the NCO groups of d to the hydroxyl and/or amino groups in the sum of a to c being between 0.9 and 1.0, characterized in that the oligomers have been prepared by employing at least one compound having 3 to 4 amino groups and having a number-average molecular weight of more than 4000 to 10,000 and/or at least one compound having 2 amino groups and having a number-average molecular weight of more than 4000 to 10,000, and in that the oligomers have double bond contents of from 0.25 to 0.44 mol/kg.